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山形大学紀要（工学）第15巻 第2号 昭和54年2月
Bull. of Yamagata Univ., Eng., Vol. 15, No. 2, Feb. 1979

Molecular motion of polybutadiene studied by ^{13}C NMR relaxation measurements

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(Received September 28, 1978)

Abstract

The ^{13}C NMR spin-lattice relaxation times (T_1) and Nuclear Overhauser Enhancement Factors (NOEF) have been measured for polybutadienes (PB) with different microstructures, namely, cis-1, 4, trans-1, 4, and equibinary cis-trans-1, 4, in solid state and in solution as a function of temperature. Measurements of ^{13}C T_1 on solid cis-trans PB show different temperature dependence for cis and trans units. The motion of cis units is influenced by the structure of succeeding monomeric units, whereas that of trans units is independent of chain structure. It is concluded that the mean number of structural units in independently moving chain segments is strongly reduced. Up to 94 ℃ the reduced values of NOEF are observed. The data are analysed in terms of the log-χ^2 distribution. This distribution gives a good fit but a too small activation energy. In order to obtain the exact distribution, the spectra of correlation times have been obtained from the ^{13}C and ^{1}H data with the aid of the principle of time-temperature reduction, where the Arrhenius equation is used as the shift factor.

Introduction

The high segment mobility of cis PB is revealed by relatively large values of ^{13}C T_1. In solid state, spin-lattice relaxation times which are comparable to what is observed for dipolar dominated relaxation in solutions of modest sized molecules are observed at room temperature [1] [2]. In many cases, the ^{13}C relaxation behavior of rigid molecules of low molecular weight can be satisfactorily described by an isotropic motional model involving a single correlation time, whereas the description of segmental motions of polymers in terms of this model is, at best, an approximate one. In the case of the ^{13}C relaxation of flexible cis PB, the model fails completely to explain the data. If the segmental motion of cis PB is isotropic, $T_1=T_2$ (the spin-spin relaxation time) and the maximum

NOEF of 2.0 are expected for this highly mobile molecular system. However, the T_1/T_2 ratio of ca. 12 and the reduced NOEF of 1.4 were observed at 35 ℃ [1]. T_1 is mainly determined by high-frequency motions, while T_2 is determined by low- frequency ones such as reorientation of relatively large chain segments. Since the NOEF depends primarily on T_1-like processes, the observed deviation appears to require the presence of some motions associated with correlation times which are long compared to those determining T_1, but short compared to those determining T_2. In fact, Schaefer [1] was obliged to use a broad asymmetric distribution of correlation times to explain the values of T_1, T_2 and NOEF. The log-χ^2 distribution used by him gave a reasonably good fit between observed and calculated values. The width of the distribution was related to the number of degrees of freedom involved in the main-chain segmental motion, and hence suggested to be a relative measure of the extent of cooperative segmental motion. On the basis of his analysis, he concluded that the segmental motion of cis PB is highly cooperative. The usefulness of the distribution was checked by Gronski and Murayama [3], but they did not refer to the cooperative motions in cis PB. However, these results whilst of considerable importance, were limited to only two temperatures and obtained taking no account of a low accuracy of the T_2 values measured directly from the line width. The former was also pointed out by Heatley and Begum [4] who made ^{13}C T_1 and NOEF measurements over a range of temperature for poly (methylmethacrylate), polystyrene and poly (propyleneoxide) in solution. They interpreted the data in terms of three models, namely, the Cole-Cole distribution, the log-χ^2 distribution, and a conformational jump model of chain dynamics. The result suggested that a description of the ^{13}C relaxation of polymers should be in terms of a distribution of correlation times or a non-exponential correlation function. This conclusion is a little surprising, because the distribution calculated from the non-exponential correlation function is utterly different from other distributions mentioned above.

In this paper we will present the results of transient NOEF experiments on PB in solid state over a temperature range between 40 and 95 ℃. The ^{13}C T_1 and NOEF data are analysed by using the log-χ^2 distribution. In order to obtain information about the exact distribution, the spectra of correlation times are calculated from the ^{13}C and ^1H data with the aid of the principle of time-temperature reduction.

Experimental

Polybutadiene samples were commercial products, which were supplied to us by Chemische Werke Hüls AG, Marl. These polymers were subjected to T_1 and NOEF measurements after purification. The T_1 values were determined from partially relaxed Fourier transform spectra with the standard 180^0- t -90^0 pulse

method at 22.63 MHz with a Bruker WH 90 pulse spectrometer. The repetition time of the pulse cycles was about five times of the longest T_1 of samples. NOEF was measured by a transient method[5]. As usual for ^{13}C T_1 and NOEF measurements on polymers[1] [3] the samples were not degassed.

Results and Discussion

A cis-1,4 polybutadiene (cis PB), an equibinary cis-1,4- trans-1,4 polybutadiene (cis-trans PB), and a polybutadiene of a high trans content (trans PB) were

Tab. 1 Microstructure of polybutadiene samples

	cis-1,4	trans-1,4	1,2-vinyl	mol %
cis PB	97			
cis-trans PB	48	47	5.0	
trans PB	13	80	7.0	

Tab. 2 Spin-lattice relaxation time T_1 and Nuclear Overhauser enhancement factor NOEF of polybutadiene at 22.63 MHz

Polymer		temp °C	T_1 (sec) a) CH	T_1 (sec) a) CH_2	NOEF b) CH	NOEF b) CH_2
cis PB	solid[c]	35	0.60	0.40	1.40	1.40
			0.58[d]		1.40[d]	
	solid	54	1.14	0.72	1.60	1.60
	solution	54	3.00	2.26	1.50	1.40
cis-trans PB	solid		0.59	0.43	1.50	1.55
cis		54				
	solution		2.30	1.65		
trans	solid		0.62	0.39	1.50	1.45
trans		54				
	solution		2.53	1.29		
trans PB	solid	80	1.14	0.69		
	solution	54	2.36	1.20		

a) Accuracy is ± 10 % , b) Accuracy is ± 0.1

c) Results of J. Schaefer[1], d) Values fitted by using the log-χ^2 distribution with b=1000, p= 9 and $\bar{\tau}$=8.3[1]; The observed T_2, 0.048 sec, and the calculated T_2, 0.042 sec.

investigated. The microstructure of these samples is shown in Tab. 1. From the ^{13}C NMR spectrum of cis-trans PB the microstructure of this sample was found to be random. The results of T_1 and NOEF measurements in solid state are shown in Fig. 1 and Fig. 2. For selected temperatures the values of T_1 and NOEF in solid state and in 20 % solutions of $CDCl_3$ are listed in Tab. 2.

At first, we compare the spin-lattice relaxation times from the standpoint of the chain structure of cis and cis- trans PB samples. We see that the T_1 values of cis units are shortened by the insertion of trans units in a cis PB chain. This holds true for solutions of PB as well as for solid PB. Since the measuring temperatures are in the high temperature side of the T_1 minimum, which is not observed by our experiments, we can conclude that the insertion of trans units in a cis PB chain reduces the mobility of cis units. On the other hand, the mobility of trans units is not affected by the insertion of cis units. The T_1 values of methine and methylene carbons of trans PB at 80 ℃ lie on the corresponding lines of cis trans PB. As it is seen in Tab. 2, no remarkable influeuce of primary structure on the T_1 values of trans units is observed. If we inquiere the

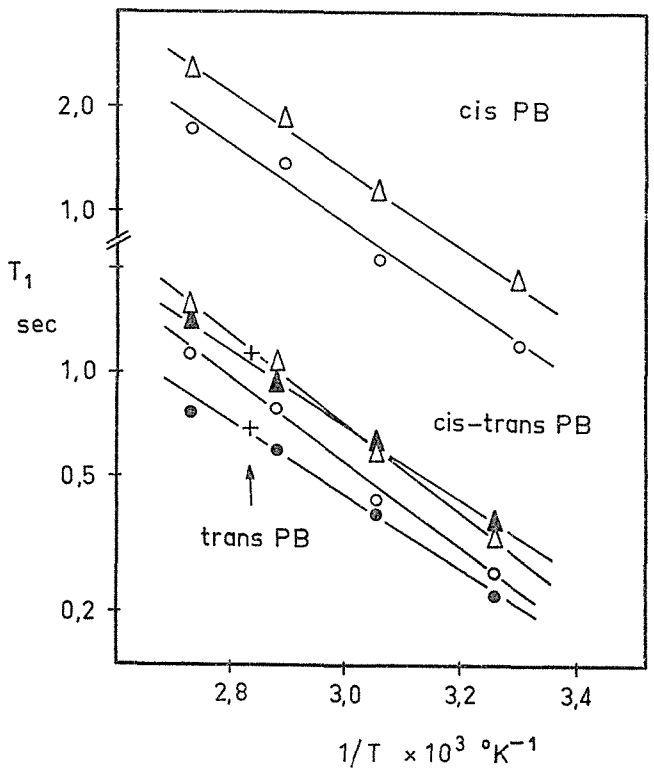

Fig. 1　^{13}C T_1 for solid PB. CH (△) and CH_2 (○) of cis units; CH (▲) and CH_2 (●) of trans units; +, trans PB

temperature dependence of T_1 of cis-trans PB in the upper half of Fig. 1, we find a difference between cis and trans units. The slop of the log T_1 *vs.* 1/T plot of cis units is steeper than that for trans units. Thereby, the lines of methine and methylene carbons of each unit run parallel each other. This is also true for the temperature dependence of CH and CH_2 groups in cis PB. However, their slopes are slightly different from those of cis units in cis-trans PB. They run almost parallel to the lines of trans units. Since cis-trans PB is an equibinary sample with a random microstructure, the observed structural effect could not appear, if the ^{13}C spin-lattice relaxation would be determined by cooperative motions of chain segments consisted of more than some monomeric units. In other words, the average number of monomeric units in a chain segment which moves almost independently of neighbouring segments is strongly reduced. In the investigation of the pressure dependence of ^1H relaxation of cis PB Geissler [6] has reached to a similar conclusion. From the slope of the log T_1 *vs.* 1/T plot the apparent activation energy was obtained. The results are

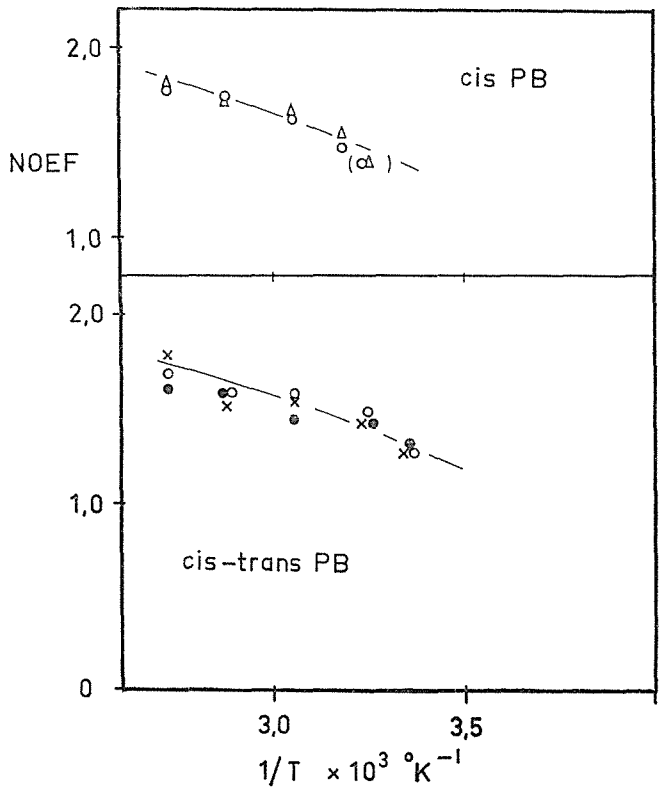

Fig. 2 NOEF for solid PB. CH (×) of cis-trans PB, other simbols as for Fig. 1. Values in parentheses are the results of J. Schaefer [1]

5.0±0.2 Kcal/mol for cis PB and trans units in cis-trans PB

6.0±0.2 Kcal/mol for cis units in cis-trans PB.

With increasing temperature the values of NOEF approach to their theoretical maximum 2.0[6]. However, unlike the maximum NOEF expected for highly mobile PB molecules, the reduced values of NOEF are observed up to 94 ℃. The values of NOEF for cis PB and cis-trans PB show similar temperature dependences and seem to be insensitive to microstructure.

In terms of spectral densities $J_{k(\omega)}$ ^{13}C T_1 and NOEF for a $^{13}CH_n$ group are given by the formulae[2]

$$T_1^{-1} = n\frac{\gamma_C^2\gamma_H^2\hbar^2}{10r_{CH}^6}\left[J_{0(\omega H-\omega C)} + 3J_{1(\omega C)} + 6J_{2(\omega H+\omega C)}\right] \quad (1)$$

$$\mathrm{NOEF} = 3.976\left[\frac{6J_{2(\omega H+\omega C)} - J_{0(\omega H-\omega C)}}{J_{0(\omega H-\omega C)} + 3J_{1(\omega C)} + 6J_{2(\omega H+\omega C)}}\right] \quad (2)$$

where γ_H and γ_C are the magnetgyric ratios of ^1H and ^{13}C, respectively, and r_{CH} is the CH bond length. It is assumed that ^{13}C relaxation occurs solely by intermolecular dipole- dipole interaction with the attached protons, and this is true for PB[7]. The spectral densities $J_{k(\omega)}$ are the Fourier transforms of the normalized autocorrelation functions of the second-order spherical harmonics of the CH bond orientaion angles:

$$J_{k(\omega)} = \int_0^\infty \overline{F_{k(\tau)}^2 F_{k(0)}^2}\, e^{i\omega\tau} d\tau \quad (3)$$

If the reorientation of the bond vector is isotropic, $F_{k(\tau)}^2$ is an exponential function with a single correlation time, i.e., $F_{k(\tau)}^2 = \exp(-|\tau|/\tau_c)$. Then $J_{k(\omega)}$ becomes:

$$J_{k(\omega)} = \frac{\tau_c}{1+\omega^2\tau_C^2} \quad (4)$$

This spectral density function is first derived by Bloembergen, Percull, and Pound[8], and hence the relaxation theory with this spectral density function is often called the BPP theory. Although the BPP theory enables us to calculate the T_1-τ_c relationship and to predict the minimum value of T_1, it can not tell us, for example, at what temperature the minimum will occur unless, of course, we know the dependence of τ_c on temperature.

In order to obtain information about the temperature variation of whatever physical process produces the fluctuations, it is usually assumed that the relationship between τ_c and T follows the Arrhenius equation

$$\tau_c = \tau_0 \exp(E/RT) \quad (5)$$

where τ_0 is the frequency constant and E the activation energy for the process. Combined with eq. (5) the BPP theory has been applied to the NMR relaxation

in polymers, however, it has failed, in many cases, to explain the experimental data. As pointed out by many workers [1,3,4,9,10], many studies of polymers by dielectric and mechanical loss methods, as well as NMR techniques, have been interpreted by assuming that the molecular motions involved have time scales which differ by many orders of magnitude, and hence are better described by a distribution of correlation times. A distribution of correlation times has also been used as a formal way of expressing a non-exponential correlation function. For a distribution of correlation times, with distributibution function $g_{(\tau c)}$ then eq, (4) becomes:

$$J_{k(\omega)} = \int_0^\infty \frac{\tau_c}{1+\omega^2\tau_C^2} g_{(\tau c)}\, d_{\tau c} \qquad (6)$$

Several workers in recent year [1,3,4] have used the log-χ^2 distribution:

$$g_{(s)}\, dS = \frac{1}{\Gamma_{(p)}} (pS)^{p-1} \exp(-pS) \qquad (7)$$

with $S = \log_b [1 + (b-1)\tau_c/\bar{\tau}]$

where $\bar{\tau}$ is the average correlation time. The log-χ^2 distribution is an asymmetric distribution having greater density for very long correlation times than for very short ones. If the parameter b is sufficiently large, this distribution is practically determined by $\bar{\tau}$ and the width parameter p. The larger p, the narrower the distribution, for $p \geqq 100$, the distribution is so narrow as indistinguishable from the BPP case. Schaefer [1] showed that the T_1, T_2, and NOEF values of PB are best fitted by using the log-χ^2 distribution (ref. Tab. 2). This was confirmed by Gronski and Murayama [3]. However, these results whilst of considerable importance, were limited to only two temperatures, and obtained taking no account of a low accuracy of the T_2 values measured directly from the line width. In the high-resolution ^{13}C NMR spectra contributions to line broadening from inhomogenity of magnetic field are inevitable. These contributions may give too small values of T_2.

Therefore, we determined two parameters $\bar{\tau}$ and p only from the T_1 and NOEF data over a range of temperature. There was little difficulty in fitting the data to the distribution. The temperature dependence of $\bar{\tau}$ is consistent with that of the width parameters, i.e., $\bar{\tau}$ becomes shorter and the distribution becomes narrower as the temperature increases; this is as expected. Greater thermal activity will lead to higher segment mobility and greater independence of succesive units, i.e., less inequality between the correlation times for different types of motion. However, it became clear after examining the results of fitting that this distribution is not suitable for PB. The activation energy of cis PB determined from the Arrhenius plot of average correlation times was 4.5 Kcal/mol. This value is about the same as the apparent activation energy of cis PB, and too

small for a system with a broad distribution of correlation times. From the temperature-frequency dependence of ^1H T_1 for cis PB, which gives the apparent activation energy of 4.9 Kcal/mol, an empirical non-exponential correlation function has been obtained by Lenk [11]. By using this correlation function and the Arrhenius equation the activation energy was found to be 9.8 Kcal/mol. It has also been shown [12] that the property of the distribution calculated from the empirical correlation function is utterly different from that of the log-χ^2 distribution. The distribution has a maximum at $\tau_c = 0$ and the tail to longer correlation times. These results indicate that the interpretation of the NMR data in terms of the distribution of correlation times and the use of a distribution as a formal way of expressing a non-exponential correlation function have a limit.

Therefore, it is very interesting to find a method which enables us to determine the exact distribution of correlation times from the experimental data for PB. For ^1H relaxation Miyake [13] has proposed a method. We summarize his method in following. The ^1H spin-lattice relaxation time T_1 is given by [8]

$$T_1^{-1} = \frac{2}{3}\gamma_H^4\sigma^2\left[\int_{-\infty}^{\infty}\frac{a_{(\tau)}\tau}{1+\omega^2(a_{(\tau)}\tau)^2}I_{(\tau)}\,d\log\tau + 4\int_{-\infty}^{\infty}\frac{a_{(\tau)}\tau}{1+4\omega^2(a_{(\tau)}\tau)^2}I_{(\tau)}\,d\log\tau\right] \qquad (8)$$

where σ^2 is the second moment of absorption line contour in the angular frequency scale. In this expression the distribution is given in log scale because of the mathematical and analytical comfortableness. The function $I_{(\tau)}$ is often called the spectrum of correlation times and related to the distribution of correlation times $g_{(\tau)}$ by the relationship $I_{(\tau)} = 2.393\,\tau\,g_{(\tau)}$. If the following approximation is made for the Debye- Bloembergen function

$$\frac{\tau_c}{1+n^2\omega^2\tau_C^2} = \begin{cases}\tau, & \tau \leqq 1/n\omega\\ 0, & \tau > 1/n\omega\end{cases}$$

and then the upper limits of integral are replaced by their geometrical average, eq. (8) can be written as

$$T_1^{-1} = 1.448\,\gamma_H^4\sigma^2\,a_{(T)}\int_0^{1/\sqrt{2}\omega a_{(T)}} I_{(\tau)}\,d\tau \qquad (9)$$

Consequently

$$I_{(1/\sqrt{2}\omega a_{(T)}=)}\ \frac{1}{\gamma_H^4\sigma^2}\frac{\omega}{T_1}\left(1+\frac{d\log T_1}{d\log a_{(T)}}\right) \qquad (10)$$

This method can be extended to ^{13}C relaxation without difficulties. The result is

$$I\left(1/\sqrt[3]{\omega_c(\omega_H^2-\omega_C^2)}\,a_{(T)}\right)=2.303\frac{r^6}{\gamma_C^2\gamma_H^2h^2}\frac{\sqrt[3]{\omega_c(\omega_H^2-\omega_C^2)}}{T_1}\times\left(1+\frac{d\log T_1}{d\log a_{(T)}}\right) \tag{11}$$

In the original work of Miyake the WLF equation was applied to $a_{(T)}$. However, the applicability of the WLF equation is practically limited to long range cooperative chain motions in the glass transition region. At high temperatures the temperature dependence of relaxation processes is governed by more specific features of chain molecules such as chemical structures. For example, Ferry and his coworkers[14] have found for ethyl-, butyl-, hexyl- and octylmethacrylates that their flexible side groups provide an additional Arrhenius term to the WLF equation. With increasing chain mobility the contribution of the Arrhenius term to $a_{(T)}$ becomes more dominant, and at high temperatures even the motion of main chains shows the Arrhenius like temperature dependence. The temperature-frequency dependence of the T_1 minima of cis PB fails to agree satisfactorily with the WLF equation if one uses the glass temperature T_g and the constants that are generally applicable to the equation[15]. A reasonably good fit between the NMR data and the WLF equation can be obtained only by using that $T_g=-125$ ℃, i.e., about 15 ℃ lower than the real glass temperature.

On the basis of these facts we assume for $a_{(T)}$ the temperature dependence of Arrhenius type, that is,

$$\tau_{(T)}=a_{(T)}\tau_{(T_S)} \tag{12}$$

with

$$a_{(T)}=\exp\{E(1/T-1/T_s)/R\}$$

$$\tau_{(T_S)}=\tau_0\exp(E/RT_s)$$

where T_s is the reference temperature.

In order to calculate $I_{(T)}$ by using eqs. (10), (11) and (12), T_1 measurements in a large temperature-frequency range are required. Our results for PB are, however, limited to only a single frequency and a small temperature range, and hitherto no ^{13}C T_1 data which cover a larger temperature range have been reported. On the other hand, the ^1H relaxation of PB is being investigated very actively. The temperature, frequency, and pressure dependences of T_1 [6,11,15], which make the estimation of E and T_s possible, as well as the influence of micro- structure on T_1 have been investigated[15]. In the calculation of $I_{(T)}$ from the ^{13}C T_1 data we utilize the result of ^1H relaxation measurements for PB, since ^{13}C and ^1H relaxations are governed by similar physical processes viz. the reorientation of the C-H bond and that of the ^1H-^1H dipole due to the relative motion of C-H bonds. To estimate E from the te.nperature-frequency dependence of T_1 a distributibution of correlation times or a motional model

must be set for PB. However, we have no information about it. Now we use a minimum condition, which holds true for many of relaxation theories with a distribution of correlation times[10];

$$\tau_c = \text{constant, at the } T_1 \text{ minimum} \tag{12}$$

The slop of the log τ_c vs. $1/T_{min}$ plot gives E. Thereby, the model dependent constant is irrelevant to the estimation of E. The values of T_{min} at various measuring frequencies have been read from the T_1 data of Slichter and Davis[15] and Lenk[11], and they are plotted in Fig. 3 against the inverse values of measuring frequencies $1/\omega$ ($\propto\tau$). A linear plot is obtained. This means that the

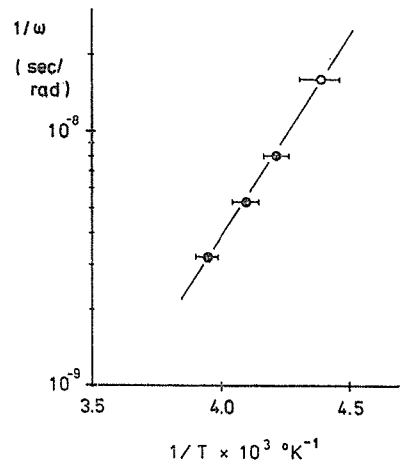

Fig. 3　Arrhenius plot of the inverse values of measuring frequencies.
● Values of Slichter and Davis; ○ Value of Lenk

segmental motions of PB show the Arrhenius like temperature dependence. The reference temperature T_s was chosen as 50 ℃ higher than the glass temperature T_g of cis PB. The second moment of cis PB was calculated according to the Van Vleck's folmula[16]. In the calculation, for simplicity, a planer zig-zag structure was assumed and the contribution of protons out of 4 Å to the second moment was ignored. The result was $\sigma^2=22.5$ gauss^2. The error due to the former assumption is at most several per cent and that due to the later assumption is not so severe because of the r^{-6} dependence of the contribution to the second moment.

The spectra of correaltion times were calculated using the values of E, T_s and σ^2 from the ^{1}H T_1 data at 30 MHz on a temperature range between ca. -100 and 100 ℃ [15] and from our ^{13}C T_1 data. In order to obtain the spectra for a

possibly wide correlation time range, linear plots of ^{13}C T_1 were assumed for a temperature range between 0 and 100 ℃. The result of calculation is shown in Fig. 4. The spectrum from the ^1H T_1 shows a maximum at $\tau_c = 10^{-8}$ sec and

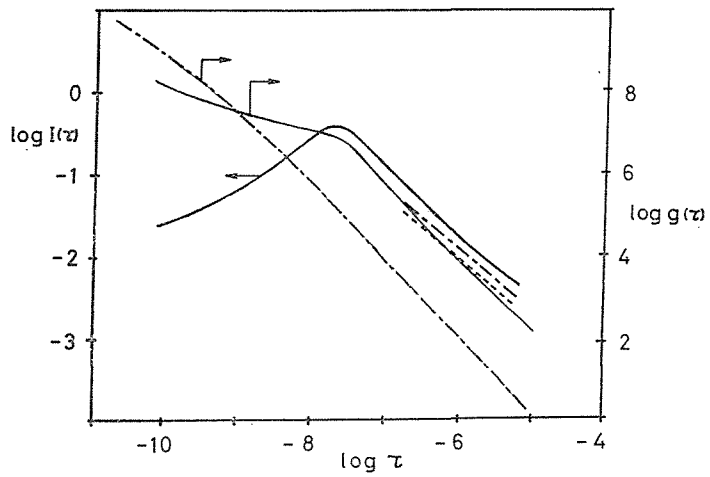

Fig. 4 Spectrum of correlation times $I_{(\tau)}$, —— from the ^1H data, — — — — from the ^{13}C data (methylene C), ····· from the ^{13}C data (methine C) ; Distribution of correlation times $g_{(\tau)}$

decreases gradually in both sides of the maximum. Only a small part of the spectrum of correlation times could be obtained from the ^{13}C T_1 data. However, it is recognaized that the spectra from the ^{13}C and ^1H data are very similar in their intensities. As it is seen in Fig. 4, $I_{(\tau)}$ curves from the ^{13}C data can be brought to coincidence with the $I_{(\tau)}$ curve from the ^1H data by small shifts along the log $I_{(\tau)}$ axis. Eqs. (11) and (12) show that the shape of the spectrum is independent of E if the log T_1 vs. 1/T plot is linear. A change of activation energy give rise to a shift of $I_{(\tau)}$ along the log $I_{(\tau)}$ axis. Since translational intermolecular processes have no importance in ^{13}C relaxation, the activation energy for ^{13}C relaxation should be slightly smaller than that for ^1H relaxation. This means, according to eqs. (10) and (11), a small shift of $I_{(\tau)}$ curves from the ^{13}C data toward $I_{(\tau)}$ from the ^1H data. The distribution $g_{(\tau)}$ of correlation times was calculated from $I_{(\tau)}$ by using the relationship $g_{(\tau)} = I_{(\tau)}/2.303\tau$. $g_{(\tau)}$ is shown in Fig. 4 by the thin line. In a correlation time range between 10^{-10} and 10^{-5} sec, the distribution decreases with increasing correlation time, and shows a shulder at the maximum of $I_{(\tau)}$. For the purpose of comparing we show a log-χ^2 distibution with $p = 9$ and $\bar{\tau} = 8.3 \times 10^{-12}$ in this figure by the

once broken line. The distribution has a maximum at $\tau_c \cong 10^{-13}$, and, in the short correlation time range of the maximum, it decreases very rapidly with decreasing correlation time. It should be noted here that the log-χ^2 distribution applied to PB is not a material function, which characterizes physical properties of material. In other words, in order to interpret the relaxation data at various temperatures in terms of the log-χ^2 distribution, a different set of parameters is required. With increasing temperature the log-χ^2 distribution becomes narrower and shifts towards shorter correlation times.

Roughly speaking, in the correlation time range between 10^{-10} and 10^{-5} sec both distributions are similar in their shapes and intensities. However, for lack of information about $g_{(\tau)}$ for a correlation time range shorter than 10^{-10} sec, we can not say whether $g_{(\tau)}$ has a maximum or not. To clarify this point is very important. Hitherto, a distribution without maximum in the vicinity of the average correlation time has been considered as physically unreasonable for NMR relaxation in polymers[1] [4]. However, there are some evidences that this is not necessarily so. As referred to previously, the distribution calculated from the empirical correlation function found by Lenk has no maximum, and the non-exponential correlation function obtained by Monnerie et. al[17], which could be successfully applied to the analysis of the experimental data for poly (methylmethacrylate), polystyrene and poly (propyrene oxide) in solution, may yield a distribution without maximum. The log-χ^2 distribution indeed gives a good fit between observed and calculated ^{13}C T_1 and NOEF values of PB, but, as it is shown in this work, it has failues. As correctly pointed out by the originator [1] this distribution allows us, at best, to describe the effects of cooperative motions in polymers on NMR relaxation times only in an approximate way, i. e., distributions of Debye oscillators (such as eq. (6)) can never exactly represent cooperative motion.

Therefore, to obtain the spectrum of correlation times for a correlation time range shorter than 10^{-10} sec is of importance in the investigation of cooperative segmental motions in PB. Measurements performed for a wide temperature range and made at different measuring frequencies provide the spectrum of correlation times for a wide correlation time range.

Acknowledgments

The authors thank Dr. W. Gronski (Institüt für makromolekulare Chemie der Universität Freiburg, BRD) for many helpful discussions.

References

(1) J. Schaefer, Macromolecules. **6**, 882 (1973)

(2) A. Allerhand, D. Doddrell, and R. Komoroski, J. Chem. Phys., **55**, 189 (1971)

(3) W. Gronski and N. Murayama, Makromol. Chemie, **177**, 3017 (1976)

(4) F. Heatly and A. Begum, Polymer, **17**, 399 (1976)

(5) K. F. Kuhlman, D.M. Grant, and R. K. Harris, J. Chem. Phys., **52**, 3439 (1970)

(6) E. Geissler, J. Polym. Sci., Polym. Phys. Ed., **13**, 1301 (1975)

(7) J. Schaefer, Macromolecules, **5**, 427 (1972)

(8) N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev., **73**, 679 (1948)

(9) T, M. Connor, Trans. Faraday Soc., **60**, 1574 (1964)

(10) F. Noack and G. Preissing, Z. Naturforsch. **24** a, 143 (1969)

(11) R. Lenk, Preprint, 8th Colloquium on NMR Spectroscopy, Aachen, 1971 ; J. Phys. C : Solid St. Phys., **4**, L21 (1971)

(12) N. Murayama, Dissertation, Freiburg (1977)

(13) A. Miyake, Repts. Progr. Polym. Phys. Japan, **4**, 36 (1961)

(14) J. D. Ferry, W. C. Child Jr., R. Zand, D. M. Stern, M. L. Williams, and R. F. Landel, J. Colloid Sci., **12**, 53 (1957)

(15) W. P. Slichter and D. D. Davis, J. Appl. Phys., **35**, 3103 (1964)

(16) H. Van Vleck, Phys. Rev., **74**, 1168 (1948)

(17) B. Valeur, L. Monnerie, and J. P. Jarry, J. Polym. Sci., Polym. Phys. Ed., **13**, 675 (1975)

山形大学紀要（工学）第15巻　第2号　昭和54年2月

^{13}C NMR 緩和測定によるポリブタジェンの分子運動の研究

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異なるミクロ構造，すなわちcis－1，4，trans－1，4，等モルcis-trans－1，4，を有するポリブタジェン（PB）の固体と溶液について ^{13}C NMR スピン格子緩和時間（T_1）と核オーバーハウザー係数（NOEF）が温度の関数として測定された。固体 cis-trans PB の ^{13}C T_1 は cis,trans 単位について異なる温度依存性を示す。cis 単位の運動はそれにつながるモノマー単位の構造に影響されるが，trans 単位の運動は影響を受けない。相互に独立に動く鎖セグメント中の構造単位の平均数はきわめて低くおさえられていることが結論される。94℃ まで NOEF の最大値は観測されない。データーは log-χ^2 分布を用いて解析された。この分布はよい一致を与えるが，得られた活性化エネルギーは小さすぎる。正確な分布を得るため，^{13}C と ^{1}H データーから時間温度換算の原理を用いて相関時間のスペクトルが求められた。ここでアレニウスの式がシフト係数として用いられた。